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Relaxation Behavior in γ -Ray Irradiated Polytrifluoroethylene

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Relaxation behavior in polytrifluoroethylene irradiated by γ -ray was investigated by dynamic mechanical and dielectric measurements. The irradiation of γ -ray to polytrifluoroethylene formed the cross-linkage between chain molecules in amorphous region and disintegrated crystals. The disintegration of crystals resulted in a decrease of crystallinity and an increase of disordered regions in crystals. The relaxation observed at 50°C and 100Hz related to the micro-Brownian molecular motion in amorphous regions was shifted to higher temperature by the irradiation because of rise of glass transition temperature due to the cross-linkage. The relaxation at temperatures from -5 to +5°C and 10kHz which consisted of two components was shifted to high temperature and decreased the relaxation intensity $\Delta\epsilon$ with increasing irradiation dose. The shift of relaxation temperature and the decrease in relaxation intensity were connected to the decrease of crystallinity. The irradiated samples exhibited a large value of $\Delta\epsilon$ than that for unirradiated samples in a temperature range from -70 to -10°C. The large value of $\Delta\epsilon$ was attributed to the molecular motions in the disorder region in crystal.

KEY WORDS: Polytrifluoroethylene/ γ -Ray/ Relaxation Behavior/ Cross-Linkage/ Crystal Disintegration

INTRODUCTION

Relaxation processes in polytrifluoroethylene (PTrFE) were investigated by some authors.¹⁻⁵ Two or three relaxation processes were observed in a temperature range from -100 to 100°C. We examined dielectric and mechanical behavior for PTrFE with different crystallinity.³⁻⁵ Three relaxations designated as α , β and β' were observed in decreasing order of temperature. The α relaxation was attributed to the micro-Brownian motion of main molecular chain. It was considered that the β relaxation consisted of two components which were attributed to the local mode relaxation at higher temperature and lower frequency and to molecular motions around vacancy defects of chain end in crystals at lower temperature and higher frequency. The β' relaxation was related to molecular motions around defects in crystals due to head-to-head and tail-to-tail bonding. The relaxation behavior of two components was resolved by examining relaxation process in benzene absorbed PTrFE since the component of the β relaxation in amorphous regions vanished by absorption of benzene. It was confirmed that the component in amorphous region was due to the local mode motion. Irradiation effects on polymers are cross-linking of molecular chains, scission of the chains, formation of other functional group and disintegration of crystals. Cross-linking may raise the glass transition temperature T_g and hinder the micro-Brownian motion. The disintegration of crystals may result in a decrease of the intensity of the

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Table I. Gel fractions and densities for irradiated and unirradiated samples.

Sample no.	Dose/Mrad	Gel fraction	Density/ 10^3kgm^{-3}
1 ^a	0	0	1.967
2 ^a	20	0.92	1.968
3 ^b	0	0	2.018
4 ^b	20	0.83	2.009
5 ^b	100	0.97	1.978

^a quenched^b annealed

relaxation attributed to the molecular motion in crystals.

In this work, relaxation behavior of PTrFE irradiated by γ -ray was examined by dielectric and dynamic mechanical measurements to elucidate the relaxation mechanisms. Results were discussed in connection with irradiation effects on change in structure such as the formation of cross-linkage and disintegration of crystal.

EXPERIMENTAL

PTrFE supplied from Daikin Co. Ltd. was melt-pressed into films with $100\mu\text{m}$ thickness at 250°C . The melt-pressed films were cooled slowly from 250°C to room temperature or quenched into cold water. The slowly-cooled specimen was annealed at 180°C for 2h. The quenched and annealed specimens were irradiated by γ -ray from a ^{60}Co source *in vacuo* up to a dose of 100Mrad at 50°C . The irradiated sample was extracted by acetone at 56°C . Gel fractions estimated from weight of insoluble residue and that of original specimen and densities measured by buoyancy method using mixtures of tetrachloromethane and 1, 1, 2, 2-tetrabromoethane are listed in Table I. Dynamic mechanical measurements were performed by a Toyo Baldwin Model DDV-II-C Rheovibron at a frequency of 3.5Hz in a temperature range from -100 to 90°C . Dielectric measurements were made by an Ando-Denki Model TR-1C transformer bridge in a temperature range of -80 to 25°C using a three terminal electrode. Thermal properties were observed by a Perkin-Elmer 7 Series thermal analyzer.

RESULTS AND DISCUSSION

The DSC curves are shown for irradiated and unirradiated PTrFE in Fig. 1. An endothermic peak of fusion took place at 199 and 205°C for unirradiated samples 1 and 3, respectively. The peak was shifted to lower temperature and depressed in size with increasing irradiation dose. The values of melting point T_m , enthalpy of fusion H_m and crystallinity X_c estimated using the enthalpy of fusion for perfect crystal⁶ are listed in Table II. The crystallinity decreased with irradiation dose and reached a considerable low value of 6.7% for sample 5 with 100Mrad. For this sample the crystallinity was lowest in all the samples, however the density was larger than that for quenched sample 2 with 20Mrad. Crystalline regions may be disordered by the irradiation. As seen in Table I, the gel fraction for quenched sample 2 with 20Mrad was larger than

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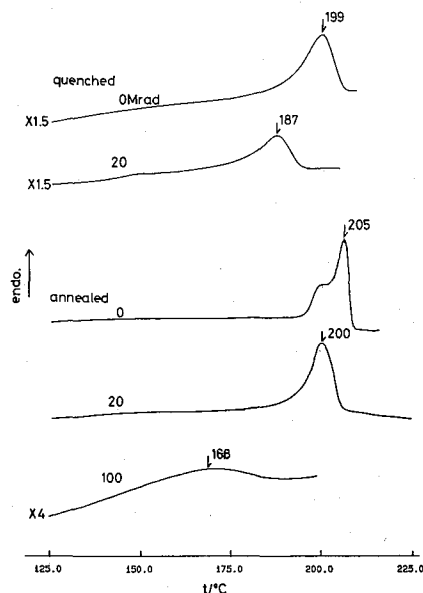


Fig. 1. DSC curves for irradiated and unirradiated samples.

Table II. Thermal properties and crystallinities for irradiated and unirradiated samples.

Sample no.	$T_m/^\circ\text{C}$	H_m/kJkg^{-1}	$X_m/\%$
1	199	17.3	25.8
2	187	11.4	17.0
3	206	23.3	34.8
4	200	19.6	29.3
5	169	4.5	6.7

that for annealed sample 4 with 20Mrad. It was confirmed that the cross-linkage was formed in amorphous regions.

The temperature dependence of mechanical loss tangent $\tan\delta$ is shown for irradiated and unirradiated PTrFE in Fig. 2. For quenched samples a large peak observed at 50°C for unirradiated sample 1, designated as α , shifted to 60°C and decreased in magnitude for sample 2 with 20Mrad. The peak for annealed sample 3 also shifted to higher temperature and depressed in magnitude at a dose of 20Mrad (sample 4). At a higher dose of 100Mrad (sample 5), the α peak moved to 100°C and recovered its intensity. As mentioned above, one of the irradiation effects is the formation of cross-linkages. The α relaxation was attributed to the micro-Brownian motion of main molecular chain because of the location of T_g at 31°C and the depression of peak size in $\tan\delta$ with increase of crystallinity.³⁻⁵ The shift of the α peak to higher temperature and the decrease of the $\tan\delta$ peak in the size with the irradiation are related to the rise of T_g and the depression of the micro-Brownian molecular motions due to the cross-linkage.

The other peak observed in a temperature range from -15 to -35°C, designated

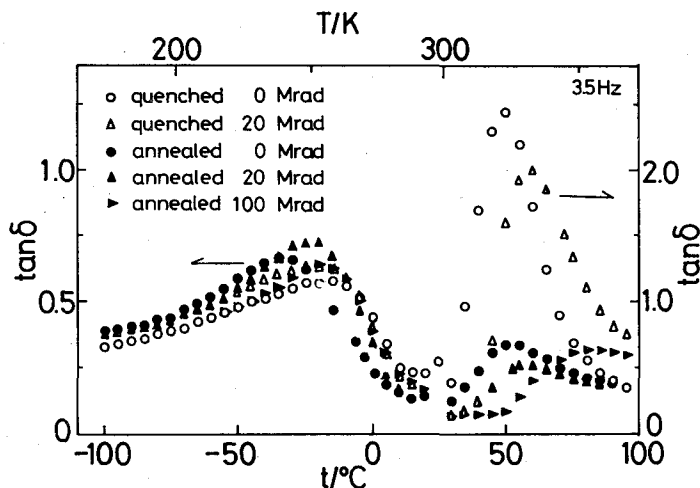


Fig. 2. Temperature dependence of mechanical loss tangent $\tan\delta$ for irradiated and unirradiated samples.

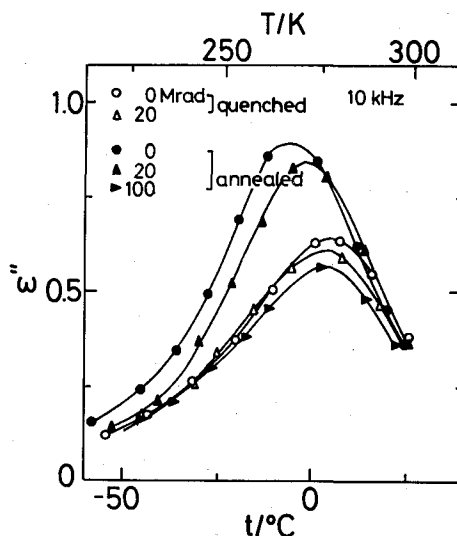


Fig. 3. Temperature dependence of ϵ'' measured at 10kHz for irradiated and unirradiated samples.

as β , shifted to higher temperature and changed in size with the irradiation. The irradiation effects on the β relaxation were also observed in dielectric properties. The temperature dependence of dielectric loss ϵ'' at 10kHz for irradiated and unirradiated PTrFE is shown in a temperature range of the β relaxation in Fig. 3. For quenched samples, the β loss peak observed at 5°C for unirradiated sample 1 was depressed slightly in size with a dose of 20Mrad (sample 2). The loss peak for unirradiated and annealed sample 3 was observed at lower temperature of -5°C than that for quenched samples 1 and 2. With increase of irradiation dose, the β peak decreased markedly in size, moved to higher temperature and reached to 5°C at 100Mrad (sample 5). The ϵ'' vs. frequency curves for annealed samples 3, 4 and 5 are shown in a temperature range

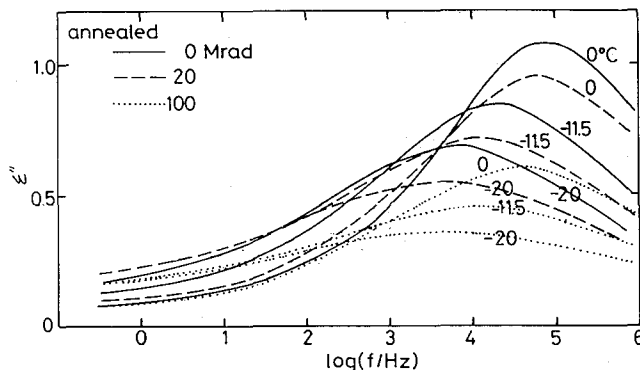


Fig. 4. Frequency dependence of ϵ'' for annealed samples with irradiation dosages of 0, 20, and 100 Mrad.

from -20 to 0°C in Fig. 4. With the irradiation the value of ϵ'' at the maximum of the curve was decreased and the relaxation frequency was shifted to lower frequency. We studied the β relaxation for samples with different crystallinity.⁵ The β relaxation decreased in size of loss peak and shifted to higher temperature with a decrease of crystallinity. Such behavior of the β relaxation was explained as follow. The β relaxation consisted of two components. One of the components, designated as β_a , was attributed to the local mode relaxation in amorphous regions and the other, designated as β_c , which took place at lower temperature and higher frequency than those for the β_a relaxation was related to the molecular motion around chain vacancy defects of chain end in crystals. Therefore the shift of the relaxation temperature and frequency and the decrease of relaxation intensity are attributable essentially to the decrease of crystallinity with the irradiation dose. Relaxation intensity $\Delta\epsilon$ in a temperature range from -10 to -70°C estimated using the Cole-Cole plot is plotted against temperatures for irradiated and unirradiated PTrFE in Fig. 5 and dependence of $\Delta\epsilon$ on crystallinity X_c is shown in Fig. 6. Values of $\Delta\epsilon$ for irradiated samples decreased with decreasing X_c and were larger than those for unirradiated samples at the same crystallinity in a temperature range from -10 to -70°C . At a temperatures below -50°C a relaxation designated as β' was observed in ϵ'' vs. frequency curves.⁵ If the irradiation introduces a new polar group into molecular chains other than C-F group in amorphous regions, $\Delta\epsilon$ for the local mode relaxation in irradiated samples is larger than that in unirradiated samples. The β_a relaxation was distinguished from the β_c and β' relaxations in crystalline regions by studying relaxation behavior in PTrFE absorbed benzene which permeated amorphous regions and made the local mode relaxation vanish. The β_a relaxation took place above -50°C , while the β' relaxation was observed at a temperature range below -50°C . Irradiated samples showed also the large value of $\Delta\epsilon$ than that in unirradiated samples below -60°C . As mentioned above the irradiation disintegrates crystals and forms the disordered region in the crystal. In the previous work⁵ the β' relaxation was connected to molecular motions of disordered chains around the defects of irregular bond such as head-to-head and tail-to-tail. If the chains in the disordered region of crystals take the molecular motions similar to those around the irregular bonds, the value of $\Delta\epsilon$ for irradiated samples is larger than that estimated

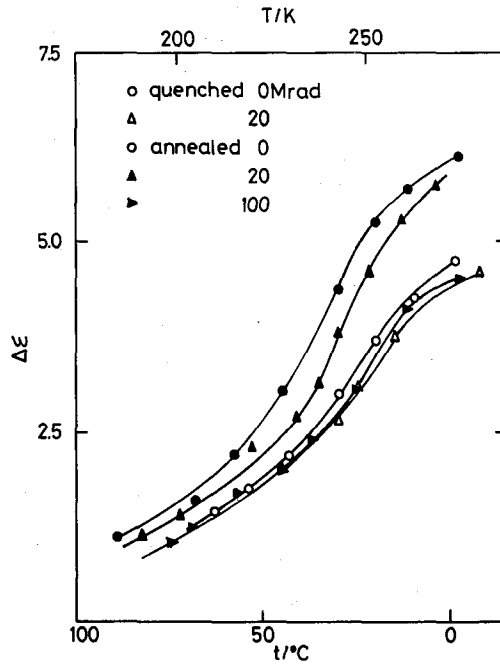


Fig. 5. Temperature dependence of $\Delta\epsilon$ for irradiated and unirradiated samples.

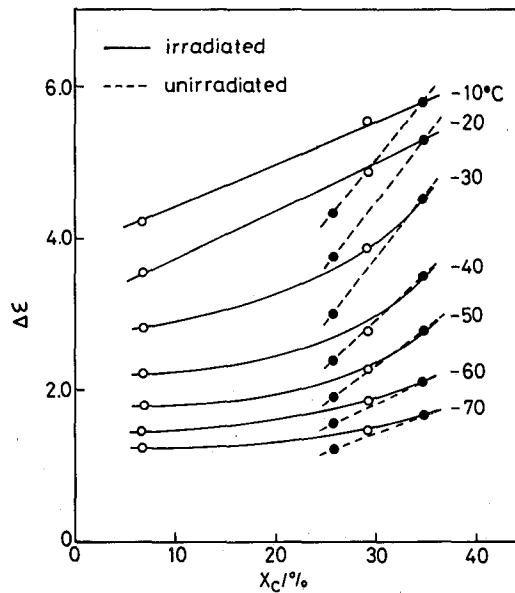


Fig. 6. Crystallinity dependence of $\Delta\epsilon$ for irradiated and unirradiated samples.

from unirradiated samples. It is likely that higher values of $\Delta\epsilon$ for irradiated samples than that for unirradiated samples at the same crystallinity is related to the increase of the disorder region formed in disintegration of crystal.

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